

RESEARCH PAPER RP884

*Part of Journal of Research of the National Bureau of Standards, Volume 16,
May 1936*

STUDIES ON THE QUATERNARY SYSTEM $\text{CaO-MgO-2CaO.SiO}_2\text{-5CaO.3Al}_2\text{O}_3$

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ABSTRACT

Determinations of primary phase volumes in the system $\text{CaO-MgO-2CaO.SiO}_2\text{-5CaO.3Al}_2\text{O}_3$ have been made. It was found that no ternary or quaternary compounds exist and that there is no detectable solid solution among any of the compounds present. A graphic illustration is shown of the amount of MgO necessary in mixtures of CaO, 2CaO.SiO_2 , and $5\text{CaO.3Al}_2\text{O}_3$ to make MgO the primary phase. This work is a necessary preliminary step in determining the effect of the state of the magnesia in portland cement.

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I. INTRODUCTION

Portland cement clinker consists essentially of lime, alumina, silica, ferric oxide, and magnesia. The last two may be generally considered as occurring incidentally, as impurities in the basic raw materials. Both serve as fluxes to lower the temperature of liquid formation, or to increase the amount of liquid formed at a given temperature, and as such are of value in manufacture. In addition, ferric oxide may confer valuable properties on the cement, which need not be considered here, and it is frequently added deliberately to the raw materials of some special purpose cements. Beyond its effect as a flux, however, magnesia has no advantageous properties and, when present in large amounts, is definitely known to be harmful. It frequently produces excessive expansion and loss of strength in concrete after one or more years. The percentage of magnesia above which it is harmful is not known precisely. Although cements which showed no unsoundness have been made containing as much as 9.5 percent of MgO ¹, the weight of evidence of tests on cements is such that practically all of the specifications used in this country limit MgO to 5 percent. The discrepancy in soundness tests on different cements containing approximately the same amounts of MgO appears to be due in part to the state in which the MgO exists in the cement.² In some cases MgO is known to occur

¹ P. H. Bates. Tech. Pap. BS. 10, (1918) T102.

² Wm. Lerch. Portland Cement Association Fellowship (Unpublished data).

as periclase (MgO), whereas, if glass occurs because of failure to attain complete equilibrium during cooling of the clinker, at least a part of the MgO must be present in the glass.

It would evidently be of considerable help in the determination of the behavior of magnesia in portland cement to establish the composition ranges within which MgO appears as a primary phase (the first phase to crystallize on cooling), but this would require the determination of a part of the equilibrium diagram of the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$. Obviously, before this can be done it is necessary to survey the systems of fewer components which comprise the boundaries of the 5-component system. The results given in this paper represent a preliminary step in this direction.

II. EXPERIMENTAL PROCEDURE

Table 1 gives the composition of the material used in this work.

TABLE 1.—*Composition of the materials used*¹

Constituents	Silica ²	Alumina ³	Magnesia ⁴	Calcium carbonate ⁵
	Percent	Percent	Percent	Percent
SiO_2	99.62	-----	0.004	-----
Al_2O_334	99.995	-----	-----
Fe_2O_302	0.05	-----	-----
MgO	-----	-----	>99.8	-----
H_2O (soluble).....	-----	-----	.15	-----
CaCO_3	-----	-----	-----	99.96
BaCO_3	-----	-----	-----	.02

¹ Water-free basis.

² Portland Cement Association Fellowship lot 3. Analyzed by H. C. Stecker.

³ Baker lot 11,528. Analyzed by W. C. Taylor.

⁴ Baker lot 9,132. Analyzed by Chemistry Division, National Bureau of Standards.

⁵ Good lot 1,240. Analyzed by Chemistry Division, National Bureau of Standards.

Since the magnesia and alumina contain fairly large and variable amounts of water, the ignition losses were determined on the same day the mixtures were prepared. In weighing out the mixes the amount of alumina was corrected for the Al_2O_3 contained in the silica. The lime, silica, and alumina were mixed by shaking dry in a bottle, grinding in a mortar, and heating at a temperature of about $1,200^\circ\text{C}$. They were then reground, reheated at a temperature high enough to give some sintering, and then again ground. The required amounts of MgO were then added and the mixture again mixed, heated, and ground.

In some cases new mixes were made by grinding together equal amounts of two previously prepared mixes.

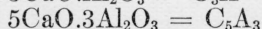
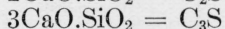
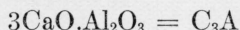
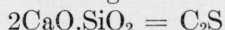
The quench method was used throughout. This method has been described by many investigators in high-temperature research so thoroughly as to make it unnecessary to go into details.³

In this work the determination of the primary phase volume of MgO and the compositions and temperatures of invariant points were the main considerations. Less attention, therefore, was paid to liquidus temperatures of compositions which were distant from invariant points.

³ G. W. Morey. *J. Wash. Acad. Sci.* **13**, 326 (1923); Shepard, Rankin, and Wright. *Am. J. Sci.* [IV] **28**, 293 (1909).

The electric furnace used was wound with 80-percent platinum—20-percent rhodium wire on a 1-inch alundum tube, and the temperature control was very like that described by Roberts.⁴ The charges were held at the required temperature for 20 to 30 minutes. A differential heating curve was used to check the temperature of the quaternary eutectic. Thermocouples were standardized at frequent intervals by quenching samples of diopside, $\text{CaMgSi}_2\text{O}_6$ (mp = $1,391.5^\circ\text{C}$) and calcium metaborate (mp = $1,154.5^\circ\text{C}$) from their melting temperatures.

In this work, as in others in this field, a short system of notations is used in referring to the compounds as follows:



Just as a ternary system is represented on a triangle with one component at each apex, so a quaternary system is best shown on a tetrahedron with one component at each apex. While in a ternary system the liquidus temperature can be shown on a curved surface a definite height above the base, this is not possible in a quaternary system. Thus, no space representation of temperature can be made. For a discussion of the tetrahedral representation of such a system reference is made to Lea and Parker⁵ and to McCaffery and co-workers.⁶

Just as the three binary systems must be known before a ternary system can be worked out, so here the four ternary systems involved must be known. These have been published^{7,8,9,10} and no attempt was made to recheck their data.

This left only an exploration of the interior of the tetrahedron. This was done by making a series of mixes containing 5 percent of MgO and determining the primary-phase volumes intersected on this plane through the tetrahedron. Then a few mixtures were made with larger amounts of magnesia to determine the amount necessary to make it the primary phase. From this work the invariant points were located tentatively and these were then more closely established by means of additional mixtures.

III. RESULTS

The composition at the invariant point at which CaO , C_2S , C_3S , and MgO are in equilibrium with a liquid and vapor could only be estimated because of the high temperatures at that region. It was estimated from the other data.

Table 2 gives the composition of the mixes and results of the quenches.

⁴ Roberts, J., *Opt. Soc. Am. & Rev. Sci. Instr.* **11**, 171 (1925).

⁵ F. M. Lea and T. W. Parker. *Phil. Trans. Roy. Soc., London* **234**, no. 731, 1 (1934).

⁶ R. S. McCaffery, J. F. Oesterle, and Leo Schapiro. *Tech. Pub. no. 19*, Am. Inst. Mining Met. Engrs. (1927).

⁷ R. A. Rankin and F. E. Wright, *Am. J. Sci. [IV]* **39**, 1 (1915).

⁸ G. A. Rankin and H. E. Merwin, *J. Am. Chem. Soc.* **33**, 568 (1916).

⁹ J. B. Ferguson and H. E. Merwin, *Am. J. Sci. [IV]* **48**, 81 (1919).

¹⁰ W. C. Hansen, *J. Am. Chem. Soc.* **50**, 3081 (1928).

TABLE 2.—Composition and results of quench mixes

Mix	Composition (in percent)				Temperature, ± 5° C	Phases present
	MgO	SiO ₂	Al ₂ O ₃	CaO		
A5.....	5.0	8.2	31.4	55.4	1,440 1,430 1,420 1,390 1,425 1,415	Glass only. Glass + CaO. Glass + CaO + C ₃ S. Glass + C ₂ S + C ₃ A. Glass + CaO. Glass + CaO + C ₃ S.
B5.....	5.0	7.1	31.1	56.8	1,503 1,500 1,480 1,450 1,400	Glass only. Glass + CaO. Glass + CaO + C ₃ S. Glass + CaO. Glass + CaO + C ₃ S.
C5.....	5.0	9.0	29.5	56.5	1,535 1,525 1,450 1,400	Glass only. Glass + C ₂ S. Glass + C ₂ S + C ₃ S. Glass + C ₂ S.
D5.....	5.0	8.0	29.5	57.5	1,450 1,400 1,385 1,375 1,375 1,360	Glass + CaO + C ₃ S. Glass + CaO + C ₃ S. Glass + C ₂ S + C ₃ A. Glass + C ₂ S. Glass + C ₂ S + C ₃ A. Glass + C ₃ A + C ₂ S.
E5.....	5.0	12.1	27.2	55.7	1,480 1,475 1,385 1,375 1,410 1,390	Glass only. Glass + C ₃ S. Glass + C ₂ S. Glass + C ₂ S. Glass + C ₃ S. Glass + C ₃ S.
F5.....	5.0	10.3	29.8	54.9	1,380 1,400 1,395 1,350 1,310 1,305	Glass + C ₂ S + C ₃ S. Glass + very small amount C ₂ S. Glass + C ₃ S + C ₃ A. Glass only. Glass + C ₃ A. Glass + C ₃ A + MgO.
G5.....	5.0	8.6	32.3	54.1	1,310 1,305 1,300 1,400 1,400 1,360	Glass only. Glass + C ₂ S. Glass + C ₂ S + C ₃ A. Glass + C ₂ S. Glass + MgO. Glass + MgO + C ₂ S + C ₃ S.
H5.....	5.0	6.9	34.7	53.4	1,390 1,380 1,350 1,310 1,305	Glass + C ₂ S. Glass + C ₃ S. Glass + C ₃ A + MgO. Glass only. Glass + C ₃ A + C ₂ S + MgO.
J5.....	5.0	9.8	29.6	55.6	1,360 1,350 1,310 1,305 1,300	Glass only. Glass + C ₃ S. Glass + C ₂ S. Glass + C ₃ A + C ₂ S + MgO. Glass only.
K5.....	5.0	7.7	33.6	53.7	1,490 1,480 1,440 1,430 1,420 1,400	Glass only. Glass + C ₂ S. Glass + C ₂ S. Glass + C ₂ S. Glass + C ₂ S + MgO. Glass + C ₂ S + MgO + C ₃ S.
L5.....	5.0	8.4	31.8	54.8	1,490 1,480 1,440 1,430 1,420 1,400	Glass only. Glass + C ₂ S. Glass + C ₂ S. Glass + C ₂ S. Glass + C ₂ S + MgO. Glass + C ₂ S + MgO + C ₃ S.
M5.....	5.0	7.4	33.4	54.2	1,395 1,350 1,340 1,370 1,360 1,340	Glass + C ₃ S + C ₃ A. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A. Glass only.
N5.....	5.0	6.6	38.5	49.9	1,330 1,310 1,305 1,300 1,350 1,310	Glass + C ₃ A + MgO. Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only.
O5.....	5.0	6.6	37.2	51.2	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
Q5.....	5.0	5.8	39.8	49.4	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
R5.....	5.0	6.5	39.5	49.0	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
S5.....	5.0	7.5	36.9	50.6	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
T5.....	5.0	6.0	40.8	48.2	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
G8.....	8.0	8.4	31.3	52.3	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
G6.5.....	6.5	8.5	31.8	53.2	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
G5.75.....	5.75	8.6	32.1	53.55	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
E10.....	10.0	11.4	25.8	52.8	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
E7.5.....	7.5	11.7	26.5	54.3	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
E6.25.....	6.25	11.9	26.9	54.95	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
U5.5.....	5.5	7.1	33.6	53.8	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.
V5.4.....	5.4	7.8	33.9	52.9	1,310 1,305 1,300 1,350 1,310 1,305	Glass only. Glass + C ₃ A + C ₂ S + MgO. Glass only. Glass + C ₃ A. Glass only. Glass + C ₃ A.

Figure 1 shows a perspective three-dimensional drawing of the quaternary system CaO-C₂S-C₅A₃-MgO. The C₂S apex lies beyond the plane of the paper. In this tetrahedron the various primary-phase boundaries are indicated. The surface intersecting the sides of the tetrahedron at A, B, C, D, E, F, and G indicates the lower level of the primary-phase volume of MgO. Thus, in all mixtures with a greater percentage of MgO than represented by this surface, MgO is the primary phase. The surface extends from 33 percent of MgO on the CaO-MgO edge to slightly under 5 percent of MgO at the quater-

nary eutectic. The lines on this surface are quintuple lines. Here five phases are in equilibrium; three solid phases, one of which is MgO , and a liquid and vapor. The dotted lines lie on the base of the tetrahedron and represent boundary curves in the ternary system $\text{CaO-C}_2\text{S-C}_5\text{A}_3$. Surfaces connecting these two sets of lines separate the primary-phase volumes of CaO , C_2S , C_3A , C_2S , and C_5A_3 .

It is seen that by far the greater part of the tetrahedron lies above the lower boundary surface of magnesia. This surface is shown in figure 2 as projected on the $\text{CaO-C}_2\text{S-C}_5\text{A}_3$ base, the eye being placed at the MgO apex. The full lines indicate the quintuple lines on this surface and the contours show the level of the surface in percentage of MgO . The contours are based to a large degree on the previously determined points on the ternary systems. The course of the con-

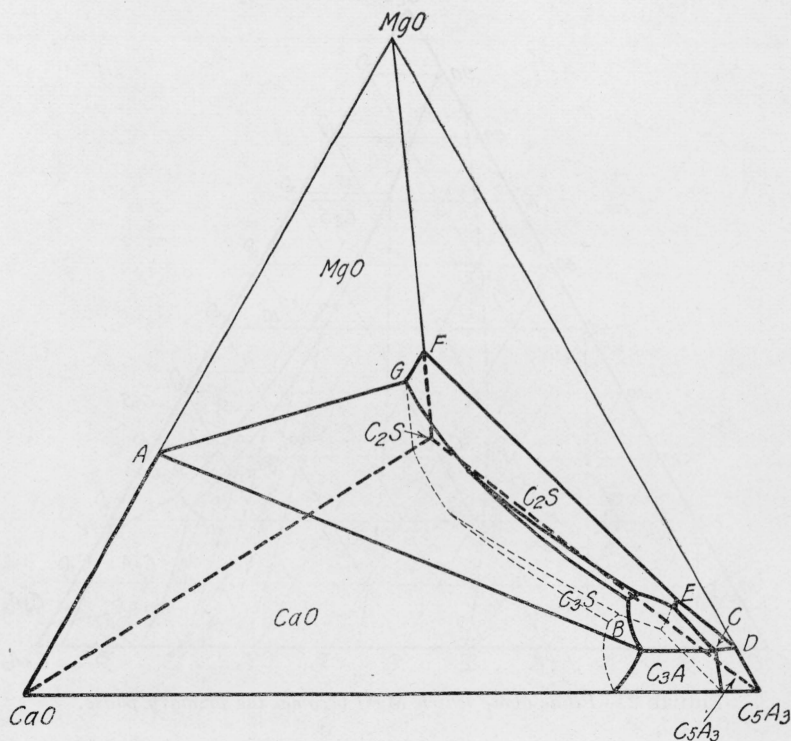


FIGURE 1.—Quaternary system $\text{CaO-MgO-2CaO.SiO}_2\text{-5CaO.3Al}_2\text{O}_3$.

tours below 10 percent is obtained from points determined near the invariant points U and V. The contour of 15 percent and those higher were largely interpolated by using the points on the sides of the tetrahedron. They were then made roughly parallel to contour lines representing lower percentages of magnesia. The relative amounts of CaO , C_2S , and C_5A_3 are shown by the triangular coordinates. These three components are thus shown on a basis of 100 percent. Therefore, a true percentage of CaO , C_2S , or C_5A_3 in a mixture on this surface is obtained by reducing the amount read from the coordinates by an amount proportional to the MgO percentage (read from the contours). The arrows on the lines indicate falling temperatures.

All the invariant points of the quaternary system lie on this surface. Thus the composition of the first liquid formed on heating any mixture of the four components will lie on this surface. The invariant points U and V are not eutectics, since they lie outside the tetrahedra bounded by the conjugation planes formed by joining the composition points of the four compounds at equilibrium at the respective points. Point W, however, is a eutectic.

The composition of most portland cements (if composed of CaO , Al_2O_3 , SiO_2 , and MgO only) would lie within a tetrahedron whose apices are the C_2S , C_3A , MgO , and C_3S composition points. Therefore, the first liquid formed on heating would be of the composition of point V and would appear at about $1,380^\circ\text{C}$. This substantiates

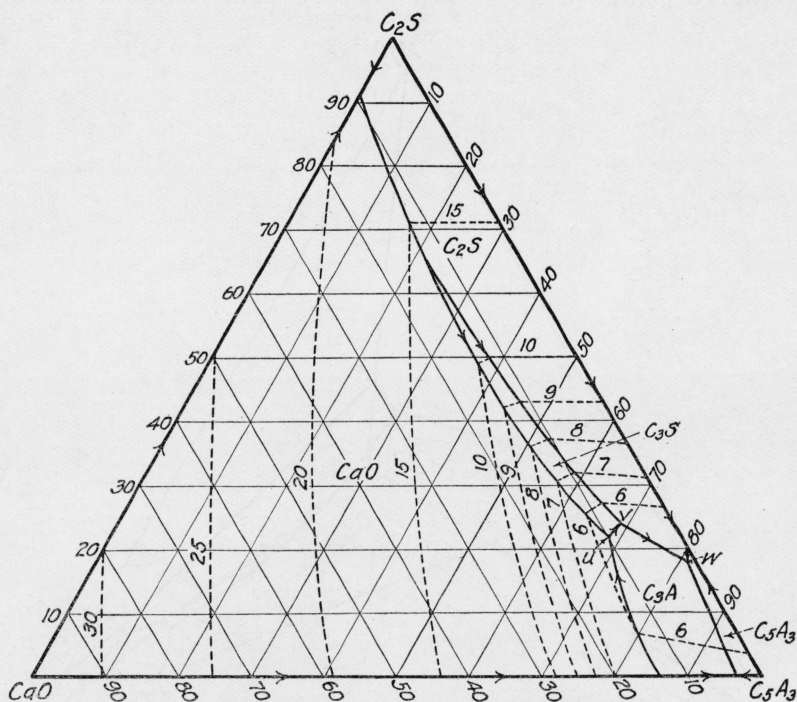


FIGURE 2.—Plane above which MgO becomes the primary phase.

the work of Hansen¹¹ in which he found that the first liquid formed on heating a portland cement mixture free from Fe_2O_3 appeared at $1,375^\circ\text{C}$. On further heating he found the invariant point corresponding to U to be at $1,395^\circ\text{C}$.

Figure 3 indicates the effect on the boundary curves of the addition of 5 percent of magnesia. The dotted lines are the boundary curves in the $\text{CaO-C}_2\text{S-C}_5\text{A}_3$ system, while the full lines indicate the position of the corresponding lines in a plane through the tetrahedron at 5 percent of MgO . The points show the location of mixes used, the compositions of which were on this plane. It must be remembered

¹¹ W. C. Hansen, B.S. J. Research **4**, 55 (1930) RP132.

that these dotted lines do not represent a ternary system, and that as soon as a compound crystallizes from a cooling liquid whose composition lies on this plane, the composition of the liquid changes in such a way that it is no longer on this level.

The binary and ternary invariant points in the tetrahedron as obtained from the aforementioned works are shown in table 3.

Table 4 is a summary of the invariant points located in the quaternary system.

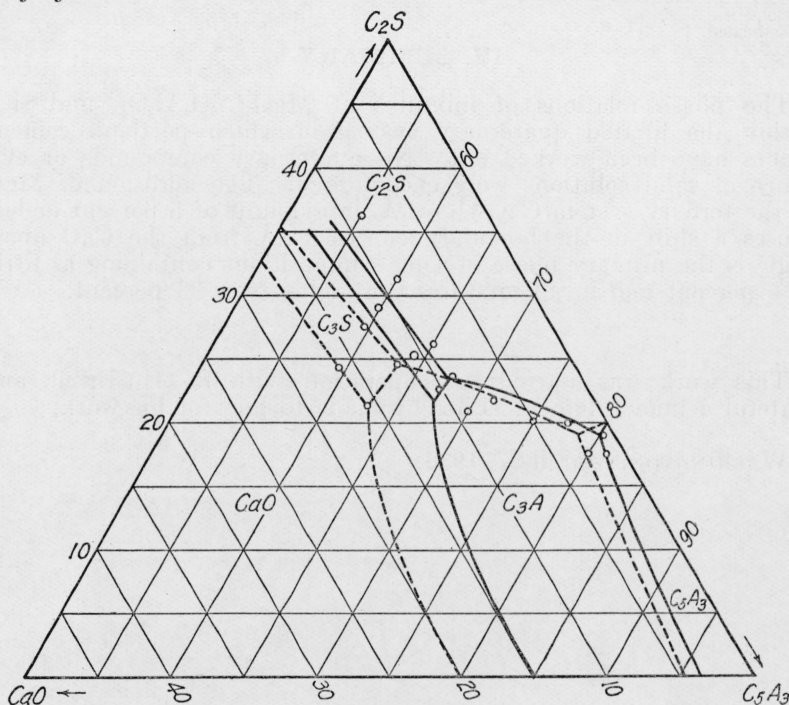


FIGURE 3.— $\text{CaO-2CaO.SiO}_2\text{-5CaO.3Al}_2\text{O}_3$ as modified by 5 percent of MgO .

Dotted lines show original boundary curves from Rankin and Wright, while full lines show boundaries with 5% of MgO added. Points indicate composition of quench mixes.

TABLE 3.—Invariant points

Liquid and vapor in equilibrium with—	MgO	SiO ₂	Al ₂ O ₃	CaO	Temperature
	Percent	Percent	Percent	Percent	°C
Binary:					
CaO-MgO ¹	33	—	—	67	2,300
C ₂ S-MgO ¹	20	28	—	52	1,925
C ₃ A ₃ -MgO ¹	6.5	—	44.5	49	1,832
C ₂ S-CaO ¹	—	32.5	—	67.5	2,065
C ₂ S-C ₃ A ₃ ¹	—	7.0	42.0	51.0	1,350
C ₃ A ₃ -C ₃ A ¹	—	—	50	50	1,395
C ₃ A-CaO.....	—	—	41	59	1,535
Ternary:					
CaO-C ₂ S-MgO ¹	19	23	—	58	1,990
C ₂ S-C ₃ A ₃ -MgO ¹	5	6.5	39.5	49	1,315
C ₃ A ₃ -C ₃ A-MgO ¹	6.3	—	47.7	46	1,345
CaO-C ₂ S-C ₃ S.....	—	22.4	9.2	68.4	1,900
CaO-C ₃ S-C ₃ A.....	—	7.5	32.8	59.7	1,470
C ₃ S-C ₃ A-C ₂ S.....	—	8.7	33.0	58.3	1,450
C ₂ S-C ₃ A-C ₃ A ₃ ¹	—	6.8	41.2	52.0	1,335
CaO-C ₃ A-MgO.....	6.2	—	42.3	51.5	1,452

¹ Eutectic.

TABLE 4.—*Quaternary invariant points*

Liquid and vapor in equilibrium with—	MgO	SiO ₂	Al ₂ O ₃	CaO	Temperature
	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>°C</i>
CaO-C ₃ S-C ₃ A-MgO-----	5.5	7.0	33.5	54.0	1,395±5
C ₃ S-C ₂ S-C ₃ A-MgO-----	5.5	7.5	34.0	53.0	1,380±5
CaO-C ₂ S-C ₃ S-MgO-----	^b 14.0	^b 19.0	^b 10.0	^b 57.0	-----
C ₃ A-C ₃ A ₃ -C ₂ S-MgO ^a -----	5.0	5.0	41.5	48.5	1,295±5

^a Eutectic.^b Estimated.

IV. SUMMARY

The phase relations of mixtures of MgO, CaO, Al₂O₃, and SiO₂ within the limited quaternary system in which portland cement occurs have been worked out. No quaternary compounds or evidence of solid solutions were encountered. The addition of MgO to the ternary system CaO-C₂S-C₃A₃ in amounts of 5 percent or less causes a shift in the boundary curves away from the CaO apex. MgO is the primary phase in some compositions containing as little as 5 percent and in all mixtures containing over 33 percent.

This work was started in cooperation with R. H. Ewell, and grateful acknowledgment is hereby made to him for his work.

WASHINGTON, March 27, 1936.